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In the present paper, we investigate the influence of additions of cadmium and divalent mercury ions on the rate of thermal decomposition of silver oxide.

The thermal decomposition kinetics was investigated by the weighing method, using a quartz balance at 300°C. The oxygen liberated in the reaction was continuously pumped off by a rotary oil pump down to a pressure of 10^{-3} mm Hg. The initial materials were silver oxide with no impurity, Ag_2O with a 10% impurity of CdO, and Ag_2O with a 5% impurity of HgO.

For addition of the impurities to the silver oxide, a mixture of 0.5N solutions of silver and cadmium in the prescribed proportions was precipitated with a 0.5N solution of NaOH. After precipitation, the preparation was dried over phosphorous pentoxide and roasted in an oxygen current at 300-315°C for an hour, after which it was treated with ozone for oxidation of metallic silver that might have formed in the preceding operation; it was then heated at 160-165°C in an oxygen current for decomposition of any higher oxides of silver that could have formed in the ozone treatment.

Silver oxide with mercury additive was prepared in similar fashion, except for the heat treatment at 300°C. The pure silver oxide was prepared by pouring 0.5N solutions of silver nitrate and sodium hydroxide together. The resultant preparation was subjected to the same treatment as the oxide with cadmium impurity, so as to preclude any possible influence of heat treatment on the

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*Numbers in the margin indicate pagination in the original foreign text.

decomposition rate. The recorded Debye patterns indicated that the addition of cadmium ions to the oxide reduces the interplanar spacings of the lattice. Consequently, the lattice of silver oxide is considerably deformed by the addition of cadmium.
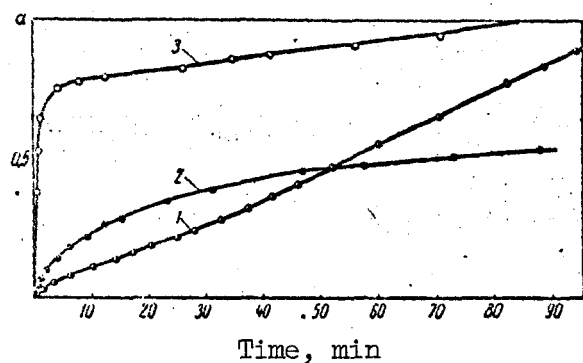

Time, min

Figure. Influence of Impurities on the Thermal Decomposition Rate of Silver Oxide:

1) Decomposition of Pure Silver Oxide; 2) Decomposition of Silver Oxide with a Cd^{2+} Impurity; 3) Decomposition of Silver Oxide Containing an Hg^{2-} Impurity.

The results of the experiments on the thermal decomposition kinetics of silver oxide are shown in the figure in coordinates α (fraction of completely reacted substance) versus t (time). It is apparent from the behavior of the curves that the thermal decomposition of pure silver oxide entails an initial small rise in the rate for the first 10 to 15 min, corresponding roughly to a 10% increment, after which the weight diminishes smoothly and uniformly with time. The addition of cadmium leads to an increase in the rate at first, then a retardation, such that ultimately the rate of thermal decomposition for silver oxide with cadmium impurity drops below the rate for the pure oxide. The addition of mercury tends to accelerate the thermal decomposition.

The variation of the thermal decomposition rate of silver oxide with the addition of impurities may be interpreted as follows. The additives can affect

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the rate, first, by deforming the lattice of the initial substance and, second, as the result of a change, induced by addition of the impurity, in the conditions for ionic and electronic processes contributing to the elementary stages of thermal decomposition.

The deformation of the lattice with the introduction of impurities must in general produce a rise in the rate of thermal decomposition, this rise becoming more pronounced the more the lattice is deformed.

The influence of the impurity may be depicted by thinking of the thermal decomposition mechanism of the the oxide as analogous to the decomposition mechanism of the silver halides, metal azides, and other ionic compounds (refs. 1 and 2). When the oxide is heated, electrons are detached from the anion, going over to the conduction band (or exciton state) with subsequent capture of an electron by either a cation capture center or an anion vacancy. The site of negative charge localization thus formed in the lattice will attract interstitial silver cations if Frenkel defects prevail in the lattice, or anion vacancies if Schottky defects prevail therein.

The addition of the doubly charged cadmium cation to silver oxide leads to the appearance of a large number of cation vacancies in the lattice, a fact that ought to be reflected in the rate of thermal decomposition. If Frenkel defects prevail in the lattice, the appearance of the cation vacancies should reduce their concentration (ref. 3) and thus slow down the rate of thermal decomposition. The decrease in rate of thermal decomposition may also occur for another reason. As we know, it is important with regard to the process of thermal decomposition that the probability of recombination between the electrons which fall into the conduction band and positive holes - O^- ions and O radicals - be minimized. For decomposition, therefore, these must be continuously

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withdrawn from the crystal. The cation vacancies formed in the lattice with the addition of an impurity may trap positive holes and thus prevent their diffusion to the surface and eventual removal from the crystal. The accumulation of positive holes in the crystal will increase their probability of recombination with electrons and will therefore reduce the thermal decomposition rate.

Consequently, an impurity of cadmium ions may, on the one hand, accelerate thermal decomposition at the expense of lattice distortion, on the other hand it can slow down the process as the result of cation vacancies formed in the lattice with the addition of the impurity. As a consequence of these two factors acting simultaneously, clearly, the kinetic behavior that we observed in the thermal decomposition of silver oxide will indeed take place. The addition of divalent mercury ions to silver oxide tends mainly to accelerate the process. This is probably related to the possible transition of mercury from the divalent to the monovalent state and a reduction due to this effect of the additive on the ionic and electronic processes associated with thermal decomposition.

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